OBSERVATIONS ON THE METALLIC ACIDS.

THESIS

PRESENTED TO THE FACULTY OF THE DEPARTMENT OF PHILOSOPHY OF THE UNIVERSITY OF PENNSYLVANIA IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

BY

ROY DYKES HALL, M. S.,
BURNETT JUNCTION, WIS.

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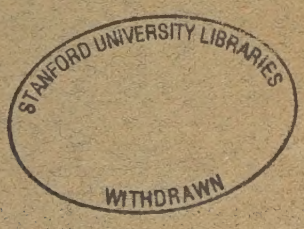

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INTRODUCTION.

This thesis presents facts observed in a study of the metallic inorganic acids. It is merely a chapter in a much larger investigation, in progress for some time, which will in due course appear in extension. The results here presented constitute but a portion of those which have been obtained.

They are preliminary in character but of distinct value in the various lines which this research has taken and along which it has been and will be carried in the future.

OBSERVATIONS ON THE METALLIC ACIDS.

The knowledge which chemists have of columbium and its derivatives as distinct from those of tantalum is due largely to the admirable researches of Marignac. He was able to obtain the columbic oxide free from oxides of tantalum, tin and tungsten, but knew of no method of testing for traces of titanium and was unable to certify as to the freedom of the columbic acid used by him, in his investigations, from this impurity.

Since the discovery of the very delicate reaction of solutions of titanium dioxide with hydrogen peroxide by Schörr the presence of traces of titanium can be readily detected.

Krüss and Nilson[1] found that by continued boiling of a dilute solution of neutral fluoxycolumbate of potassium, a small portion of the columbium separated, the spark spectra of which showed none of the lines characteristic of titanium. Others as Osborne[2] and Larsson[3] have succeeded in obtaining columbium sufficiently pure, so that it would not respond to the hydrogen peroxide test for titanium, by recrystallization of the double fluoride.

It was desired to test the method of obtaining pure columbium and to compare the reactions of potassium columbium fluoride with those of the double fluorides of such elements as are liable to occur with it.

The atomic weight of columbium was determined by Marignac

[1] Ber. d. chem. Ges., 1887, 1676.
[2] Amer. Jour. Science [3], 30, 331.
[3] Ztschr. anorg. Chem., 12, 188.

by the analysis of the fluoxycolumbate of potassium, and direct comparison of potassium sulphate to columbic oxide. As the fluoxycolumbate of ammonium is changed to oxide on careful ignition this salt was studied with regard to the ease of preparation and definiteness of constitution with a view of using it in the determination of the atomic ratio of columbium.

The mineral from Haddam, Conn., was very iridescent. pounds of columbite from the Black Hills, S. D., and 25 pounds of columbite from Haddam, Conn.

The mineral from Haddam, Conn., was very iridescent, lamellar, brittle and ground to a brown powder inclined to reddish. Its specific gravity compared with water at 4° C. was 5.750.

Weight of mineral	5.6515
Weight of pyknometer + water	39.7061
	45.3576
Weight of pyknometer + mineral + water	44.3779
	0.9797

$t = 26°$.

	Analysis.	
	I.	II.
$Ta_2O_5 + Cb_2O_5$	79.75	79.49
$WO_3 + SnO_2$	0.32	0.32
Fe_2O_3	15.11	15.09
U_3O_8	0.23	0.24
MnO	6.69	5.83
	102.10	100.97

For analysis the finely powdered mineral was fused with 8 to 10 parts of potassium bisulphate for about thirty minutes. The fusion was taken up in hot water and boiled until decomposed, then filtered and washed with hot water. The oxides were treated with yellow ammonium sulphide on the filter; after washing out the ammonium sulphide, the iron and manganese remaining as sulphides were dissolved out with dilute sulphuric acid. The dilute sulphuric acid washings were added to the original filtrate.

The sulphides soluble in ammonium sulphide were precipitated by hydrochloric acid and after ignition weighed as oxides.

The filtrate from the oxides of columbium and tantalum, to-

gether with the dilute sulphuric acid washings, was evaporated to small bulk and ammonium carbonate in excess added, followed by ammonium sulphide to precipitate iron and manganese and leave uranium in solution. Uranium was tested for in the filtrate from the sulphides of iron and manganese by destroying the ammonium carbonate with hydrochloric acid and then adding a slight excess of ammonium hydrate. After standing forty-eight hours a slight precipitate came down; it gave the characteristic chromium bead.

The mineral from the Black Hills, South Dakota, was black, with nearly a metallic luster. It was tougher than the Haddam variety and was not iridescent.

Sp. gr. compared with water at 0° C.	5.861
$t = 24°$.	
Mineral	8.9402
Pyknometer + water	39.7232
	48.6634
Pyknometer + water + mineral	47.1422
	1.5212

	Analysis.	
	I.	II.
$Cb_2O_5 + Ta_2O_5$	81.05	80.98
$SnO_2 + WO_3$	0.25	0.28
Fe_2O_3	7.61	7.65
U_3O_8	....	0.11
MnO	12.92	....
	101.83	

The oxides of tantalum and columbium, obtained from all of the analyses, were white and did not change in weight upon a second fusion with bisulphate, nor was any iron or manganese extracted.

The South Dakota mineral to the amount of 21.3 kilos was fused with 58.5 kilos of potassium bisulphate, 100 grams of the mineral being fused at a time. The method followed for the oxides was the usual one where decomposition is affected by fusing with bisulphate.

5.87 kilos of picked material were obtained from the Haddam

mineral. It was ground fine enough to pass through a 120 mesh sieve and decomposed by fusing with potassium acid fluoride, according to the method suggested by Gibbs[1] for the decomposition of this mineral. A platinum dish of about 300 cc. capacity was used for the fusions. One hundred grams of mineral were mixed with from 200 to 210 grams of potassium fluoride, the whole made to a thin paste with hydrofluoric acid and dried out on a stove plate, after which the fusions were made with a four-burner Bunsen and a blast-lamp. The preparation of a charge for fusion required about one hour, while five to ten minutes were sufficient to insure complete decomposition of the mineral, which was indicated by the flux becoming pink.

In working up the fusions it was found impracticable to extract with water, acidulated with hydrofluoric acid, as had been intended, because of lack of vessels of sufficient capacity. The fusions were, therefore, ground up, put into shallow lead dishes, about 12 inches wide and 2 deep, covered with water and decomposed with two to three times their weight of concentrated sulphuric acid. The heating was done on a sand-bath and continued until the excess of acid had distilled off.

On extracting the mass with boiling water the oxides of columbium and tantalum remained insoluble, together with oxides of silicon, titanium, tungsten, tin and any lead sulphate formed by the action of the acids on the lead vessels. These oxides were washed until the washings no longer gave a precipitate with ammonium hydrate. They were then covered with a concentrated solution of yellow ammonium sulphide and allowed to stand for several days.

After the ammonium sulphide was drawn off the oxides, now black from iron sulphide, were washed well with water, then with dilute sulphuric acid, to remove the iron. It was hoped that this treatment would remove the stannic and tungstic acids and the remainder of the bases, leaving only the oxides of silicon and titanium and sulphate of lead with the columbium and tantalum.

The oxides were dissolved in hydrofluoric acid and the lead sulphate filtered out. The hydrofluoric acid solution was made

[1] Amer. Jour. Science, **37**, 357 (1864).

of such a concentration that on the addition of its equivalent of potassium fluoride most of the tantalum and silicon fluorides present separated as double fluorides with potassium fluoride. These were filtered out and dried. The filtrate was evaporated in large rubber dishes over a water-bath, a slight excess of potassium fluoride being added. If more of the needles of potassium tantalum fluoride separated they were added to the first crop.

The remaining double fluorides were taken out in two fractions, the first one being largely potassium columbium oxyfluoride, the last one containing the same, together with the excess of potassium fluoride. The weights of the fractions obtained were:

	Kilos.
$K_2TaF_7 + K_2SiF_6$	1.250
K_2CbOF_5	1.800
$K_2CbOF_5 + KF$	1.325
Total	4.375

About 100 grams of the middle portion, consisting, for the most part, of potassium columbium fluoride, was recrystallized four times, after which it gave a precipitate with hydrogen sulphide. Sufficient of this sulphide was collected to test, and it was found to consist largely of sulphide of tin.

A solution of the salt was brought to boiling, and hydrogen sulphide passed into saturation, then filtered and the filtrate tested by diluting and again passing in hydrogen sulphide, with negative results. Upon evaporation of the filtrate to crystallization and analyzing a portion of the crystals obtained, the resulting columbic oxide stained the platinum crucible. Upon taking the crystals up in water and passing in hydrogen sulphide more sulphide of tin was obtained. It was found impossible to remove all of the tin with hydrogen sulphide even upon crystallizing five times, taking up the crystallizations in water and passing in hydrogen sulphide through the solution each time.

The salt remaining after the above treatment was crystallized twice and analyzed.

(1) 0.5508 gram gave 0.2522 gram Cb_2O_5, and 0.3288 gram K_2SO_4, giving an atomic weight of 93.4 for columbium.

(2) 0.5105 gram gave 0.2342 gram Cb_2O_5 and 0.3044 gram K_2SO_4, or an atomic weight for columbium of 93.8.

In both cases the platinum crucible used for the ignition of the oxide was stained noticeably.

Marignac pointed out that tin and tungsten were not completely removed by hydrogen sulphide from an acid solution of the double fluoride, but it seemed quite probable that they should be from a neutral solution.

It had previously been considered sufficient to wash the hydrated oxides well with yellow ammonium sulphide in order to remove the oxides of tin and tungsten, for Pennington[1] had shown the considerable solvent action exerted on the oxides of columbium and tantalum by digesting with yellow ammonium sulphide. Washing with ammonium sulphide having failed to remove all of the tin, and tungsten digestion was reverted to.

Five hundred grams of the double fluorides were changed to oxide by decomposing with sulphuric acid and extracting the oxides with boiling water. The oxides thus obtained were digested with yellow ammonium sulphide on a water-bath for twenty-four hours, the ammonium sulphide solution decanted, and a fresh portion added. This was repeated four times, and each of the ammonium sulphide solutions were precipitated with hydrochloric acid, filtered and the precipitate ignited.

In each case a considerable residue was obtained. The residue from the first two were combined and reduced in hydrogen in a Rose crucible. The tin was then dissolved out with hydrochloric acid, precipitated with ammonium hydrate, filtered, ignited and again reduced. About 1 gram of metallic tin was obtained. Its solution in hydrochloric acid reduced mercuric chloride solution, gave purple of Cassius with a solution of gold chloride and gave a brown-black sulphide, soluble in yellow ammonium sulphide.

The part insoluble in hydrochloric acid was ignited, fused with potassium bisulphate and extracted with boiling water. Upon digestion of the hydrate thus obtained with ammonium hydrate a large amount went into solution. After filtering, the filtrate gave a precipitate with acids, but the precipitate was white, not yellow, and did not get yellow after long boiling. There was

[1] J. Am. Chem. Soc., 18, 38.

every evidence that the precipitated tungstic acid contained columbic acid and that, on digesting the mixed hydrate with ammonium hydrate, a complex acid had been formed. Long boiling with strong acid was required to precipitate all of the oxide from this solution.

These oxides were filtered out and, after igniting, fused with sodium carbonate. Upon taking up in water, the sodium carbonate was nearly insoluble in the excess of alkali and could be filtered out. The addition of acid to the filtrate gave a yellow precipitate which answered to all the tests for tungstic oxide.

That part which was insoluble in ammonia was also fused with sodium carbonate and likewise found to contain both columbic and tungstic oxides. This would indicate that a separation of the mixed hydrates of columbium and tungsten by digestion with ammonium hydrate is impossible.

The oxide obtained from the fourth digestion with ammonium sulphide was found to contain both tin and tungsten, so the oxides were washed free from ammonium sulphide, then again digested with fresh ammonium sulphide, with the result that a fresh amount of stannic and tungstic acids was extracted. This seemed to bear out the statement of H. Rose, that the oxide of tin and tungsten could not be removed by digestion with ammonium sulphide, so recourse was had to the method adopted by him, namely, fusion with sodium carbonate and sulphur.

The flux used was three parts sulphur to two parts sodium carbonate and three parts of this was taken for one of the oxide. The fusions were made in a porcelain crucible at a temperature below that at which sodium carbonate would fuse.

Upon extracting with water, the columbic oxide remained insoluble as an acid sodium salt; the tin and tungsten going into solution were filtered off and the oxide washed with a solution of sodium sulphide.

The acid sodium salt was ignited and changed to the oxide by fusion with potassium bisulphate and extracting with boiling water to remove the sodium and potassium sulphate. A portion tested for tin and tungsten by a second fusion with sodium carbonate and sulphur failed to show their presence.

The columbic oxide was converted into double fluoride by dissolving in hydrofluoric acid, adding its equivalent of potassium fluoride, and the double fluoride separated by successive evaporations.

The crystals obtained were dried in an air-bath and then hydrogen sulphide passed through their solution to remove traces of lead introduced with the potassium fluoride. The solution was also boiled in the hope of removing the remaining tantalum.

These double fluorides were crystallized twice, taking only the first portions, and 125-150 grams thus obtained. Each time the dried crystals were taken up in water and boiled a slight residue separated; this was tantalum. In order to remove all of the tantalum the double fluoride was heated to 150°-175° in an air-bath, then, on dissolving, a considerable residue remained. Upon repeating this twice a tantalum-free preparation was obtained.

The potassium columbium oxyfluoride was tested for titanium by the hydrogen peroxide test. As this is not delicate in the presence of fluorides the solution was changed to chloride, and in the following way: The double fluoride was decomposed with sulphuric acid, the oxide well washed, then boiled for a few minutes with concentrated hydrochloric acid, after which it was soluble on diluting or in water. Titanium was tested for in this solution by adding hydrogen peroxide and some was found.

The color developed by hydrogen peroxide was first used by Weller[1] for the quantitative estimation of small amounts of titanium. He used it to determine titanium in the presence of zirconium, and suggested that it would answer equally well in the presence of columbium, but he did not test this suggestion. Osborne[1] used the method, working in chloride solutions.

Another crystallization was made, only the first fraction being taken; this was well washed and, tested for titanium, showed its presence in amount nearly equal to that in the first sample. The lack of improvement in amount of titanium, shown in successive crystallization, made it evident that titanium could not be completely eliminated from columbium by a limited number of crystallizations.

[1] Ber. d. chem. Ges., **7**, 1882, 2592.
[2] Amer. Jour. Science [3], **30**, 329.

The columbium was changed to the normal double fluoride and this crystallized in the hopes that, not being isomorphous with potassium titanium fluoride, it might separate free from that impurity. Four crystallizations were made from a fairly concentrated hydrofluoric acid solution, then some of the columbium converted to chloride and tested with hydrogen peroxide. It was found to contain less titanium, the amount having decreased by one-half.

The columbium was changed to oxyfluoride by crystallizing twice from water, the mother-liquors discarded and the crystals dried in an air-bath at 150°. They were analyzed according to the method used by Marignac.

0.5684 gram gave 0.2659 gram of oxide and 0.3485 gram of K_2SO_4, showing an atomic weight for columbium of 92.8.

The delicacy of the hydrogen peroxide test for titanium was studied, together with the effect of the presence of various substances on its delicacy.

0.1017 gram of potassium titanium fluoride, containing 0.03356 gram of oxide, was changed to sulphate and made up to 100 cc. One cc. contained 0.00003356 gram TiO_2. One-tenth of this solution, or 0.000003356 gram TiO_2, showed a color with hydrogen peroxide when made up to 50 cc. in a Nessler tube of one-inch diameter.

The most dilute standard solution which could well be used for comparison work would be 2 cc. of the above in 50 cc., or 0.00067 gram TiO_2 in 50 cc., each cubic centimeter containing 0.000013 gram TiO_2. With such a solution the successive comparisons against an unknown did not vary over 2 cc., or 0.000026 gram of TiO_2. This agrees fairly well with that found by Weller, who gave the limit of the method as 0.1 mg. in 1 cc.

A solution of potassium titanium fluoride, containing 0.00128 gram of TiO_2, had a color developed by hydrogen peroxide equal in intensity to that given by 0.000318 gram in sulphate solution, or a loss of color due to the presence of fluoride of about three-fourths.

The intensity of the color given by hydrogen peroxide with titanium is much lessened by the presence of citric acid, but is

not noticeably affected by oxalic or tartaric acid. This permits of the use of the oxalate or binoxalate solution of tantalum and columbium in the making of the tests for titanium.

The moist hydrates of tantalum and columbium, as well as of titanium, are readily soluble in potassium binoxalate to stable solutions from which they are precipitated by an excess of ammonium hydroxide.

Five-tenths gram of potassium tantalum fluoride was decomposed by sulphuric acid and the hydrate dissolved in potassium binoxalate; it showed no color with hydrogen peroxide. Upon the addition of 0.00015 gram of TiO_2, a color was produced which was matched by a solution containing 0.000147 gram of titanic oxide, showing that the tantalum does not interfere with the color test for titanium in potassium binoxalate solution. The percentage of titanic oxide in the potassium columbium oxyfluoride was determined by destroying the fluoride and dissolving in potassium binoxalate. The tin- and tungsten-free sample, after two crystallizations, showed oxide of titanium to be about 0.5 per cent. of the total oxide; after the four crystallizations from hydrofluoric acid the amount was reduced to 0.25 per cent.

It was noticed by Smith[1] that sulphur monochloride dissolved the oxides of columbium, tantalum and titanium, in the first two cases forming crystalline bodies and with the oxide of titanium a liquid. It was hoped that by a further study of this reaction a method might be found which would eliminate the traces of titanium from the columbium.

Oxide of titanium, heated in a sealed tube with sulphur monochloride at 200° for several hours, went into solution, and when the contents of the tube were transferred to a distilling bulb the titanium was volatilized with the sulphur monochloride, probably as the tetrachloride. Oxide of columbium, under the same conditions, went into solution in the sulphur monochloride and separated from it on cooling in transparent yellow prisms, of what was later found to be the pentachloride. On transferring to a distilling bulb the sulphur monochloride could be distilled off and then the columbium chloride distilled over into the stem of the distilling bulb, sealed off and analyzed.

[1] J. Am. Chem. Soc., **20**, 289.

The chloride of columbium came over between 220° and 235°. Prepared in this way, it was difficult to free from sulphur monochloride. After several failures a sample was obtained containing only a small amount of sulphur and analyzing as follows:

0.4400 gram gave 0.2160 gram Cb_2O_5 and 1.1380 grams AgCl, or 0.2815 gram Cl.

0.5395 gram gave 0.2690 gram Cb_2O_5 and 0.0195 gram $BaSO_4$, or 0.0027 S.

	Calculated for $CbCl_5$.	Found.	
Cb	34.62	34.7	
Cl	65.38	64.0	
S	....	0.5	
	100.00	99.2	
Cb_2O_5	49.35	49.8	49.1

The analysis was made by decomposing the sample with dilute ammonia water, evaporating to small bulk and filtering off the columbic hydrate after neutralizing the excess of ammonia with nitric acid. The chlorine was determined in the filtrate. The second sample was decomposed with water and the sulphur oxidized with bromine water, and the filtered hydrate was washed with dilute ammonium hydrate to remove all the sulphuric acid. Any oxide of columbium adhering to the glass was dissolved off with potassium binoxalate, or by boiling with concentrated hydrochloric acid and again precipitated by ammonium hydrate.

In order to see if titanium could be removed from columbium by means of sulphur monochloride, 1.1 grams of columbic oxide, containing 0.25 per cent. of oxide of titanium, was heated with sulphur monochloride in a sealed tube for fourteen hours.

The contents of the tube were transferred to a distilling bulb and distilled. The sulphur monochloride and the oxide carried with it were decomposed by ammonia water and the ignited oxide tested for titanium. 0.0955 gram obtained were found to contain 0.00066 gram of titanic acid, or 0.7 per cent.

The sublimed crystals of columbic chloride were changed to oxide and 0.4295 gram found to contain 0.00075 gram of TiO_2, or 0.18 per cent., showing only a slight improvement.

The desire to prepare the chloride of columbium free from

oxychloride and sulphur monochloride lead to an attempt to change the oxide to chloride by heating in a current of sulphur monochloride, and distilling the resulting chloride in a current of chlorine.

Under these conditions the ignited oxide was rapidly changed to chloride at a moderate temperature and with a small amount of sulphur monochloride. Oxychloride was at first formed, but this changed rapidly in the sulphur monochloride vapors to chloride. On cutting out the sulphur monochloride and substituting a current of dry chlorine gas the columbium pentachloride could be distilled and freed from sulphur, as the following analyses show:

(1) 0.6290 gram $CbCl_5$ gave 0.3105 gram Cb_2O_5; 1.6590 grams ClgCl, or 0.2178 gram Cb and 0.4101 gram Cl.

(2) 0.4084 gram $CbCl_5$ gave 0.2021 gram Cb_2O_5; 1.0788 grams AgCl, or 0.1418 gram Cb and 0.2658 gram Cl.

	Calculated.	Found. I.	Found. II.
Cl	65.38	65.20	65.33
Cb	34.62	34.63	34.71
	100.00	99.83	100.04
Cb_2O_5	49.35	49.26	49.49

The silver chloride obtained was perfectly white and showed no trace of sulphide.

The chloride of tantalum was prepared in a similar way; because of its higher boiling-point it is easier to free from sulphur monochloride than is the columbium body.

It was obtained in nearly white crystals, fusing to a light yellow oil. It was analyzed by decomposing in dilute ammonia, allowing to stand twenty-four hours, then adding nitric acid in slight excess, which caused the tantalic hydrate to flocculate and filter readily. Cl was determined in the filtrate.

1.4684 grams of $TaCl_5$ gave 0.9085 gram Ta_2O_5; 2.9215 grams AgCl, or 0.7454 gram Ta and 0.7228 gram Cl.

	Calculated for.	Found.
Ta	50.76	50.77
Cl	49.24	49.22
	100.00	99.99
Ta_2O_5	61.86	61.87

The ease with which these two difficultly reducible oxides were changed to chlorides in a current of sulphur monochloride vapor lead to a series of qualitative experiments to see what oxides would be so changed and if certain quantitative separation might not be affected by the use of sulphur monochloride, also if various minerals might not be readily decomposed by means of it.

It was found that the oxides of titanium, aluminum, iron, besides columbium and tantalum were readily changed to volatile chlorides at a moderate temperature.

Oxides of tungsten, vanadium and molybdenum were changed to volatile oxychlorides.

Oxides of zirconium and tin were changed to volatile chlorides, but exposure to a temperature approaching the softening-point of soft glass for a considerable time was required for complete transformation.

Oxides of boron and silicon were not affected, while chromic oxide was changed to the slightly volatile violet chloride. Oxides of manganese, sodium and those oxides forming non-volatile chlorides were changed to chlorides, the chlorides remaining in the boat and being soluble in water.

Some of the columbite from the Black Hills, S. D., was readily decomposed, the tantalum, columbium and iron being volatile and leaving manganese chloride sufficient in weight to give 13 per cent. MnO—that obtained in the analysis was 12.92 per cent.

Chromite was changed to volatile ferric chloride and the violet chromium chloride, which, calculated to oxide with the gangue, gave 46 per cent. remaining in the boat.

The titanium in rutile was completely expelled, the iron and titanium in ilmenite were driven out, leaving a white residue. All of the titanic oxide was volatilized from a mixture of titanic and silicic acids.

The use of sulphur monochloride affords an excellent and convenient method of preparing the anhydrous chloride of many of the elements. It offers a means of separating those forming volatile chlorides from those forming non-volatile chlorides. It

also affords an excellent means of decomposing some of the most refractory of minerals.

The use of sulphur monochloride having failed to remove the last traces of titanium from columbic oxides, the method of Krüss and Nilson was tested. The recrystallized potassium columbium oxyfluoride was taken up in water and boiled for a long time, replacing the water lost by evaporation. A small amount of an acid salt separated. When sufficient was obtained it was washed thoroughly, then changed to oxide by fusion with bisulphate of potassium and the oxide dissolved in hydrochloric acid and tested with hydrogen peroxide. 0.32 gram showed the presence of 0.00015 gram TiO_2, or 0.05 per cent., the best that had been obtained.

As this method was essentially a fractional precipitation it was thought probable that other more rapid methods of a similar nature might accomplish the same result.

According to Demarçay,[1] all of the columbium is precipitated from a solution of the double fluoride of potassium and columbium by making the solution exactly neutral with ammonium hydrate and boiling, while titanium is not precipitated until an excess of ammonia has been added. Following this suggestion, a solution of fluoxycolumbate of potassium was made nearly neutral with ammonium hydrate in the cold. The ammonia was added in dilute solution, and with constant stirring to prevent an excess at any one point for an appreciable length of time.

The hydrate thus precipitated was dissolved in hydrofluoric acid and the operation repeated.

0.1473 gram of this oxide in hydrochloric acid solution showed no yellow with hydrogen peroxide, while the addition of 0.00003 gram titanic acid gave the characteristic color for titanium. The amount of titanium present, therefore, was materially less than 0.02 per cent.

When the precipitation was made from a boiling solution some titanium was brought down with the columbium hydrate. From precipitations made in this way, starting with oxyfluoride con-

[1] *Compt. Rend.*, 100, 740.

taining 0.5 per cent. of titanium oxide, gave a product containing about 0.1 per cent. of the titanium oxide. Subsequent precipitations from a boiling solution failed to decrease this amount.

Four precipitations in the cold, precipitating one-half to three-fourthsof the columbium present each time, gave a titanium-free hydrate.

QUALITATIVE TESTS.

Potassium titanium fluoride was prepared from rutile by fusing the finely powdered mineral with three times its weight of potassium fluoride, according to the method suggested by Gibbs. The fusions were ground up and the potassium titanium extracted with boiling water, acidulated with a few drops of hydrofluoric acid. Sixty grams of rutile yielded 130 grams of the recrystallized double fluoride.

Analysis:

(1) 0.7365 gram gave 0.2392 gram TiO_2 and 0.5174 gram K_2SO_4.

(2) 0.9722 gram gave 0.3193 gram TiO_2.

	Calculated.	Found.
TiO_2	33.33	32.5–32.8
K_2SO_4	72.50	70.2

The sample taken from analysis was air-dried and not perfectly anhydrous. The atomic weight of the titanium, as obtained by comparison with TiO_2 with K_2SO_4, is 48.4.

The solution used for the following tests contained 5 grams of salt to 400 cc. of water.

NaOH—Precipitation complete.

Na_2CO_3—Precipitation complete.

$KHCO_3$—No precipitate in the cold; on boiling a precipitate formed; it was not complete.

$(NH_4)_2CO_3$—No precipitate in the cold; standing twenty-four hours gave a slight precipitate.

$BaCO_3$—(Emulsion) precipitation complete in the cold.

KCN—Precipitation complete.

KCNS—A crystalline precipitate is formed on the addition of a centrated solution of potassium thiocyanate.

K_4FeCN_6—No precipitate.

K_3FeCN_6—Crystalline precipitate.

K_2CrO_4—Heavy precipitate, insoluble in water, nearly complete.

$K_2Cr_2O_7$—No precipitate.

KI—Potassium titanium fluoride is much less soluble in a solution containing potassium iodide than in water. The crystals, which separate, carry down a large amount of potassium iodide. 1.5 grams of potassium titanium fluoride were dissolved in 37.5 cc. of water, then 112.5 cc. of a cold saturated solution of potassium iodide added; the whole brought to boiling, when it became clear; on cooling, a heavy crop of feathery crystals separated. These were sucked dry with a filter-pump and then put between filter-paper and analyzed. 0.8408 gram gave 0.1273 gram AgI, or 0.0899 gram KI and 0.2320 gram TiO_2, or 0.6960 gram K_2TiF_6. K_2TiF_6 = 82.8 per cent.; KI = 10.6 per cent.; water by difference = 6.6 per cent.

KBr—The same as potassium iodide. One part of potassium titanium fluoride is soluble in 500 parts of potassium bromide solution, containing 240 grams of KBr. The potassium titanium fluoride separating from such a solution carries down about 10 per cent of KBr.

KIO_3—Precipitation complete on using an excess of the reagent and boiling vigorously.

$KBrO_3$—No precipitate.

$KClO_3$—No precipitate.

$KClO_4$—No precipitate.

$NaPO_3$—No precipitate.

$Na_4P_2O_7$—No precipitate.

Na_2HCO_4—Precipitation complete.

Na_2SO_3—Heavy precipitate on boiling not complete; no precipitate from acid solution.

$Na_2S_2O_3$—Slight precipitate formed slowly; was soluble in acids.

$(NH_4)_2SO_4$—No change.

K_2SO_4—No change.

H_2SO_2—Yellow color.

$AgNO_3$—No precipitate.

$HgNO_3$—No precipitate.

$HgCl_2$—No precipitate.

Pb acetate—Heavy precipitate; soluble in nitric acid.

$BaCl_2$—Slight precipitate, becoming heavy and flocculent on boiling; soluble in acids.

Alcohol—An equal volume of 95 per cent. alcohol precipitated nearly all of the double fluoride.

Oxalic acid—No precipitate.

NH_4 oxalate—No precipitate.

Acetic acid—No precipitate.

Na acetate—Heavy precipitate, on boiling, nearly complete.

Fumaric acid—No precipitate; excess of ammonia precipitates.

NH_4 fumarate—No precipitate; precipitate on boiling.

Formic acid—No precipitate.

NH_4 formate—Precipitate forms slowly; nearly complete on long boiling.

Maleic acid—No precipitate.

NH_4 maleate—No precipitate; boiling precipitates.

NH_4 citrate—No precipitate; excess of ammonium hydrate does not precipitate.

Salicylic acid—No precipitate; excess of ammonia precipitates.

Succinic acid—No precipitate; excess of ammonia precipitates.

Malic acid—No precipitate; large excess of ammonia gives a precipitate.

Benzoic acid—No precipitate.

Na benzoate—Precipitate in the cold; not complete on boiling.

Tartaric acid—No precipitate prevents precipitation with ammonia.

α-Nitroso-β-naphtha (in 50 per cent. acetic acid)—No precipitate.

NH_4 tungstate—No precipitate.

NH_4 molybdate—No precipitate.

Solution of gall nuts—Neutral solution; no precipitate; red color. Hydrochloric acid solution slight; yellow color. Alkaline solution deep red color.

Zn, HCl } Sea-green.

H_2O_2—Deep yellow color.

Clean surface of Zn—After twenty-four hours the liquid was pink; after several days the zinc was covered with a dark feathery deposit.

Potassium Columbium Oxyfluoride.—Columbic oxide was extracted from columbite, as described, freed from titanium by fractional precipitation with ammonium hydrate, changed to the double fluoride with potassium and recrystallized. A solution containing 10 grams to 500 cc. was used for the following reactions:

NaOH—A precipitate was formed, nearly all soluble in slight excess; a large excess causes crystals of sodium columbate to separate; nearly insoluble in alkali.

KOH—Precipitate soluble in large excess.

Na_2CO_3—Heavy precipitate; nearly all soluble in slight excess; similar to NaOH.

$(NH_4)_2CO_3$—Precipitate; soluble in a large excess.

$KHCO_3$—Precipitate soluble in excess on standing; a slight precipitate separates.

$BaCO_3$—(Emulsion) precipitate, nearly complete in twenty-four hours in cold.

KCN—Heavy white precipitate.

KCNS—Slight precipitate in concentrated solution.

K_4FeCN_6—A yellow-green precipitate separates slowly.

K_3FeCN_6—No precipitate.

K_2CrO_4—Precipitation complete.

K_2CrO_7—No precipitate.

KI, KBr } Potassium columbium oxyfluoride is less soluble in solution of these than in water.

KIO_3—An equal volume of a hot saturated solution of potassium iodate gave no precipitate; long boiling gave a partial precipitation.

$KBrO_3$—No precipitate.

$KClO_3$—No precipitate.

$KClO_4$—No precipitate.

$NaPO_3$—No precipitate.

$Na_4P_2O_7$—No precipitate.

Na_2HPO_4—No precipitate.

Na_2SO_3—Heavy precipitate complete from neutral solution.

$(NH_4)_2SO_4$—No change.

K_2SO_4—No change.

H_2SO_2—No change; slight precipitate on long standing.

$AgNO_3$—No precipitate.

$HgNO_3$—Slight precipitate; soluble in the excess of nitric acid in the reagent.

$HgCl_2$—No precipitate.

Pb acetate—Heavy precipitate.

$BaCl_2$—Precipitate soluble in hydrochloric acid.

Alcohol—(Equal volume of 95 per cent.) heavy gelatinous precipitate.

Oxalic acid—No precipitate.

NH_4 oxalate—No precipitate.

Acetic acid—No precipitate.

Na acetate—Heavy precipitate complete in the cold.

Fumaric acid—No precipitate.

NH_4 fumarate—Precipitation practically complete on boiling.

Maleic acid—No precipitate.

NH_4 maleate—No precipitate; precipitation complete on boiling.

Formic acid—No precipitate.

NH_4 formate—Precipitation complete on boiling.

NH_4 citrate—No precipitate; prevents precipitation by ammonia.

Salicylic acid—No precipitate.

Succinic acid—No precipitate.

NH_4 acid succinate—Precipitates slowly on boiling.

Malic acid—No precipitate. Excess of ammonia gives a partial precipitation.

Benzoic acid—No precipitate.

Na benzoate—Precipitate in the cold complete on boiling.

Tartaric acid—No precipitate. Excess of ammonia and boiling does not give a precipitate at once, but on long standing a precipitate forms.

α-Nitroso-β-naphthol (in 50 per cent. acetic acid)—No precipitate.

Na tungstate—No precipitate.

NH_4 molybdate—No precipitate.

Solution of gall nuts—No precipitate, reddish color. Upon the addition of hydrochloric acid and warming, the color faded and then a precipitate formed, becoming brick-red.

Zn, HCl } Green-brown, going to a deep brown.

H_2O_2—No color.

Potassium Tantalum Fluoride.—Tantalic acid was obtained from columbite and fused with sodium carbonate and sulphur to remove the tin and tungsten, then treated with potassium fluoride and sulphuric acid to remove the silica, and changed to double fluoride. The double fluoride was crystallized four times.

0.8084 gram gave 0.4568 gram of Ta_2O_5 or 56.5 per cent.; calculated, 56.6 per cent.

The solution used for the following reactions contained 1 gram of potassium tantalum fluoride in each 150 cc. of water. A few drops of hydrofluoric acid were added to prevent the separation of an oxy salt.

NaOH—Slight permanent precipitate; not soluble in excess; crystals deposit on standing.

Na_2CO_3—Heavy precipitate, not complete.

Na_2CO_3—No precipitate; heavy precipitate on long standing.

$(NH_4)_2CO_3$—Heavy precipitate.

$BaCO_3$—(Emulsion) precipitation complete on boiling; evidently little reaction in the cold.

KCN—Precipitation complete.

KCNS—Slight white precipitate.

K_4FeCN_6—A yellow precipitate forms slowly.

K_3FeCN_6—No precipitate.

K_2CrO_4—Precipitation complete.

$K_2Cr_2O_7$—No precipitate.

KI, KBr, KCl } Precipitates the potassium tantalum fluoride.

KIO_3—No precipitate.

$KBrO_3$—No precipitate.

$KClO_3$—No precipitate.

$KClO_4$—No precipitate.

$NaPO_3$—No precipitate.

$Na_4P_2O_7$—No precipitate.

Na_2HPO_4—No precipitate.

Na_2SO_3—A precipitate forms slowly.

$Na_2S_2O_3$—Slight precipitate.

K_2SO_4—Cold saturated solution gives a heavy precipitate soluble on warming.

$(NH_4)_2SO_4$—No precipitate.

H_2SO_2—Heavy precipitate after standing some time.

$AgNO_3$—No precipitate.

$HgNO_3$—No precipitate.

$HgCl_2$—No precipitate.

Pb acetate—Heavy precipitate.

$BaCl_2$—White precipitate; soluble in hydrochloric acid.

Alcohol—No precipitate.

Oxalic acid—No precipitate.

NH_4 oxalate—No precipitate.

Acetic acid—No precipitate.

Na acetate—Boiling gives a heavy white precipitate nearly complete.

Fumaric acid—No precipitate.

NH_4 fumarate—Boiling gives a precipitate nearly complete.

Formic acid—No precipitate.

NH_4 formate—Precipitation complete on long boiling.

Maleic acid—No precipitate.

NH_4 maleate—Precipitation nearly complete on boiling.

NH_4 citrate—No precipitate; excess of ammonium hydrate precipitates slowly on boiling.

Salicylic acid—No precipitate.

Succinic acid—No precipitate.

NH_4 acid succinate—Boiling gives only a slight precipitate.

Malic acid—No precipitate; excess of ammonium hydrate in the cold gives no precipitate; boiling gives a precipitate.

Benzoic acid—No precipitate.

Na benzoate—Slight precipitate.

Tartaric acid—No precipitate; excess of ammonia precipitates slowly on boiling.

α-Nitroso-β-naphthol (in 50 per cent. acetic acid)—No precipitate.

Na tungstate—No precipitate.

NH_4 molybdate—No precipitate.

Solution of nut galls—Faint yellow color; to precipitate with hydrochloric acid; ammonia gives a brown color.

Zn and HCl—No color.

H_2O_2—No color.

Potassium Zirconium Fluoride.—One hundred and twenty grams of picked zircons were heated red hot and plunged into cold water, then ground to a fairly fine powder. Their decomposition was affected by the method used by Marignac, namely, fusion with 2.5 ot 3 parts of potassium acid fluoride. The decomposition was rapid and complete. The fusions were ground up and the potassium zirconium fluoride extracted with boiling water, the double fluoride of silicon and potassium being insoluble.

One hundred and five grams of the salt recrystallized three times was obtained.

It was analyzed according to the method of Berzelius, by ignition with sulphuric acid to $ZrO_2 + K_2SO_4$, extracting the K_2SO_4 with water, reweighing the ZrO_2 and getting the K_2SO_4 by difference. The zirconium hydrate was also precipitated by ammonium hydrate and weighed after ignition.

I. 1.0085 grams gave 0.4385 gram ZrO_2 and 0.6239 gram K_2SO_4.

II. 0.8062 gram gave 0.3500 gram ZrO_2.

III. 1.3071 grams gave 0.5725 gram ZrO_2.

		Found.		
	Calculated.	I.	II.	III.
ZrO_2	43.34	43.51	43.41	43.79
K_2SO_4	61.61	61.74	....	....

Ten grams of salt were dissolved in 500 cc. of water and this solution tested with the following reagents.

NaOH—Precipitation complete.

K_2CO_3—Precipitation slow but complete.

$KHCO_3$—No precipitate.

$(NH_4)_2CO_3$—No precipitate.

$BaCO_3$—Precipitation nearly complete in the cold.

KCN—Precipitation complete.

KCNS—A crystalline precipitate is formed on adding a concentrated solution of potassium sulphocyanide.

K_4FeCN_6—Small white precipitate.

K_3FeCN_6—A few graular crystals separated.

K_2CrO_4—Heavy white precipitate not complete; insoluble in water.
$K_2Cr_2O_7$—No precipitate.
KI—A crystalline precipitate of the double flouride separates.
KBr—Same as potassium iodide.
KIO_3—Heavy precipitate complete on boiling.
$KBrO_3$—No precipitate.
$KClO_3$—No precipitate.
$KClO_4$—No precipitate.
$NaPO_3$—No precipitate.
$Na_4P_2O_7$—No precipitate.
Na_2HPO_4—Precipitation complete.
Na_2SO_3—Precipitate formed slowly; nearly complete in twenty-four hours.
$Na_2S_2O_3$—Small precipitate.
$(NH_4)_2SO_4$—No change.
K_2SO_4—No change.
H_2SO_2—A light yellow precipitate separated slowly.
$AgNO_3$—No precipitate.
$HgNO_3$—No precipitate.
$HgCl_2$—No precipitate.
Pb acetate—Heavy precipitate.
$BaCl_2$—Precipitate soluble in hydrochloric acid.
Alcohol—Crystalline precipitate soluble on warming.
Oxalic acid—No precipitate.
NH_4 oxalate—No precipitate.
Acetic acid—No precipitate.
Na acetate—Precipitate not complete.
Fumaric acid—No precipitate.
NH_4 fumarate—Boiling precipitates.
Formic acid—No precipitate.
NH_4 formate—Precipitates on boiling but not complete.
Maleic acid—No precipitate.
NH_4 maleate—Boiling precipitate.
NH_4 citrate—No precipitate; prevents precipitation by ammonia.
Salicylic acid—No precipitate.
Succinic acid—No precipitate.
Malic acid—No precipitate; prevents precipitation by ammonia.

Benzoic acid—No precipitate.

Na benzoate—Precipitation not complete on boiling.

Tartaric acid—No precipitate; prevents precipitation by ammonia.

α-Nitroso-β-naphthol (in 50 per cent. acetic acid)—No precipitate.

NH_4 tungstate—No precipitate.

NH_4 molybdate—No precipitate.

Solution of gall nuts—A slight white precipitate in acid solution.

Zn, HCl } No color.

H_2O_2—No color.

Study of Ammonium Fluoxycolumbate.—Ammonium fluoxycolumbate was prepared from fluoxycolumbate of potassium by adding a dilute solution of distilled ammonia to a dilute solution of the double fluoride until nearly neutral. The hydrate of columbium precipitated was filtered and washed thoroughly with hot water, then dissolved in distilled hydrofluoric acid and the precipitation with ammonia repeated. The columbic hydrate was again filtered and washed, then dissolved in hydrofluoric acid, and ammonium hydrate added.

The precipitate formed was just dissolved in hydrofluoric acid and the solution evaporated to crystallization. The salt that was obtained was recrystallized twice and dried in an air-bath at 100°. It was then ground to a fine powder and heated for one hour at 150°. Analysis.

I. 0.4839 gram of the salt gave 0.3381 gram of Cb_2O_5.

II. 0.4086 gram of the salt gave 0.2867 gram of Cb_2O_5, or 69.98 per cent. and 70.17 per cent. respectively that calculated for the salt $2NH_4F.3CbOF_3$ is 69.91 per cent. Cb_2O_5. This salt contained more columbium than any of those obtained by Marignac, the nearest to it being NH_4FCbOF_3, giving 65.68 per cent. on ignition.

In order to change it to the normal double fluoride, it was dissolved in water, a considerable excess of ammonia and hydrofluoric acid added and the solution evaporated to crystallization on a water-bath. Although the solution was acid to test-paper, the vapors given off were distinctly ammoniacal.

A sample from the first crop of crystals was analyzed and found to contain 43.4 per cent. Cb_2O_5, which showed the presence of an excess of ammonium fluoride, the normal salt requiring 55.68 per cent.

The salt was then crystallized three times; each time on warming the solution the vapors were alkaline. The crystals from the third crystallization were dried in an air-bath at 110°. According to Marignac the normal salt undergoes no change in weight on heating to 170°-180°.

Upon ignition of a sample with sulphuric acid, 0.4905 gram gave 0.3355 gram of 68.5 per cent. oxide, instead of 55.68 per cent., which the normal salt $CbOF_3.2NH_4F_3$ would contain.

While any of the numerous double fluorides of potassium and columbium upon crystallization from water yield the normal oxyfluoride, it would seem that the normal oxyfluoride of columbium and ammonium is neither as easily formed nor as stable as the corresponding potassium salt.

It was found that during evaporation of the solution of an ammonium double fluoride rich in ammonium fluoride, on the water-bath, it lost ammonium, going to a salt poorer in ammonium fluoride than the normal salt.

Unless some method can be found which will yield the normal fluoride and permit of its purification without danger of changing its composition it cannot be of service in the determination of the atomic weight of columbium.

This investigation was undertaken at the suggestion of Dr. Edgar F. Smith, and I take this opportunity of sincerely thanking him for his encouragement and ready advice throughout the work.

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